

THE CALCULATION OF THE CONTRIBUTIONS TO LOW ENERGY e^+H_2 SCATTERING FROM Σ_u^+ and Π_u SYMMETRIES USING THE KOHN VARIATIONAL METHOD

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Abstract

Above incident energies of about 2 eV, the contribution to the total cross section in e^+H_2 scattering from the Σ_g^+ symmetry is insufficient to account for the experimental value. We describe calculations we have carried out of the lowest partial waves of Σ_u^+ symmetry and Π_u symmetry using the Kohn variational method. The contributions to the total cross section from the two equivalent partial waves of Π_u symmetry significantly reduce the discrepancy with experiment up to incident energies of 4–5 eV. Comparisons are made with recent R -matrix calculations performed by Danby and Tennyson¹.

Introduction

For incident energies up to about 2 eV, the contribution to the total cross section in e^+H_2 scattering from the lowest partial wave of Σ_g^+ symmetry is sufficient to account for the experimental value provided Hylleraas-type functions, containing the positron-electron distance as a linear factor, are included in the Kohn trial function². The lowest partial wave of Σ_g^+ symmetry is the analogue of the s -wave in positron or electron-atom scattering. The next symmetries from which significant contributions may be expected as the energy increases above 2 eV are the Σ_u^+ and Π_u symmetries. The lowest partial waves of these symmetries are the analogue of the p -wave in positron or electron-atom scattering. The decrease in symmetry in changing from an atomic target such as H or He to H_2 splits the p -wave between the two symmetries: the $m = 0$ component is included in the Σ_u^+ symmetry, whereas the $m = \pm 1$ component is included in the Π_u symmetry.

The asymptotic effective potential between the target hydrogen molecule and an incident positron is of the form

$$V(r) \underset{r \rightarrow \infty}{\sim} \frac{QP_2(\cos \theta)}{r^3} - \frac{\alpha_0}{2r^4} - \frac{\alpha_2 P_2(\cos \theta)}{2r^4} \quad (1)$$

r and θ are spherical coordinates of the positron measured from the nuclear centre of mass, with the z -axis along the nuclear axis. Q is the quadrupole moment of the hydrogen molecule. The first term in (1) is the asymptotic form of the static potential, first order in the interaction between the positron and the target. The other terms are of second order. α_0 and α_2 are respectively the spherical and non-spherical dipole polarisabilities of the hydrogen molecule, and are linear combinations of $\alpha_{||}$ and α_{\perp} , the dipole polarisabilities parallel and perpendicular to the nuclear axis. In second order perturbation theory, the expressions for $\alpha_{||}$ and α_{\perp} are made up of contributions from virtual excitations to states of Σ_u^+ and Π_u electronic symmetry respectively³.

The Σ_g^+ partial wave trial function used in reference 2 did not include functions with the correct asymptotic form to deal with the long-range polarisation of the molecule. However, there is evidence from Kohn calculations of e^+H and e^+He scattering that short-range exponentially decaying trial functions are adequate in the case of the s -wave except in the vicinity of zero energy^{4,5}. It is reasonable to expect that this will be the case for Kohn calculations of the lowest partial wave of Σ_g^+ symmetry in e^+H_2 scattering. There is no centrifugal barrier⁶ and the phase shift is determined by the positron-molecule interaction at all separations and not just when the positron is far from the molecule.

This is not the case for higher partial waves which experience centrifugal barriers. For sufficiently low incident energies long-range behaviour dominates and the phase shifts for these partial waves may be obtained from the first Born approximation⁷ using the asymptotic potential (1). Armour and Plummer⁸ show for e^+H_2 scattering that the correct behaviour of the phase shifts at very low energies follows naturally from the Kohn equations if the trial function includes long-range polarisation functions of the correct form.

Several authors^{5,9,10} have reported poor convergence of p -wave phase shifts at low incident energies (incident wave number $k = 0.1 a_0^{-1}, 0.2 a_0^{-1}$) in Kohn calculations of e^+H and e^+He scattering that did not include long-range polarisation functions in the trial function. Armour¹¹ found similar behaviour at low energies in a Kohn

calculation of the lowest partial wave of Σ_u^+ symmetry in e^+H_2 scattering that took no account of long-range polarisation. The trial functions for the present calculations of the lowest partial waves of Σ_u^+ and Π_u symmetries include long-range polarisation functions, separable correlation functions of Σ_g^+ , Σ_u^+ , Π_u and Π_g electronic symmetries, and Hylleraas-type functions, important at higher energies ($k > 0.1 a_0^{-1}$) for taking into account short-range interactions between the positron and the target electrons.

The Calculations

The calculations are extensions of the earlier calculations^{2,11}. Prolate spheroidal coordinates are employed in the fixed nuclei model and the open channel functions are made up of solutions to the free-particle equation in this coordinate system appropriate to the lowest partial waves of Σ_u^+ symmetry and Π_u symmetry, respectively. With Ψ_G the model H_2 ground-state wave function, the correlation functions are of the form

$$N(\lambda_1^{a_i} \lambda_2^{b_i} \mu_1^{c_i} \mu_2^{d_i} [M_1 \cos(\phi_1 - \phi_3)]^{p_i} [M_1 \cos \phi_1]^{q_i} r_{13}^{t_i} + \lambda_2^{a_i} \lambda_1^{b_i} \mu_2^{c_i} \mu_1^{d_i} [M_2 \cos(\phi_2 - \phi_3)]^{p_i} [M_2 \cos \phi_2]^{q_i} r_{23}^{t_i}) e^{-\beta(\lambda_1 + \lambda_2)} f_i(3) \Psi_G. \quad (2)$$

Coordinates 1 and 2 represent the electrons and coordinates 3 represent the positron, and

$$f_i(3) = \begin{cases} \lambda_3^{r_i} \mu_3^{s_i} e^{-\alpha \lambda_3} M_3^{p_i} [M_3 \cos \phi_3]^{u_i} & \text{(separable and Hylleraas functions),} \\ \left\{ \begin{array}{c} \sin c \lambda_3 \\ \text{or} \\ \cos c \lambda_3 \end{array} \right\} \frac{1}{\lambda_3^3} (1 - e^{-\gamma(\lambda_3 - 1)})^{w_i} \mu_3^{v_i - p_i} \left(\frac{M_3}{\lambda_3} \right)^{p_i} \left[\frac{M_3 \cos \phi_3}{\lambda_3} \right]^{u_i} & \text{(polarisation functions).} \end{cases}$$

$$M_i = [(\lambda_i^2 - 1)(1 - \mu_i^2)]^{\frac{1}{2}}.$$

$a_i, b_i, c_i, d_i, p_i, q_i, r_i, s_i, t_i, u_i, v_i$ and w_i are non-negative integers and α, β, γ and N are constants. $c = \frac{1}{2}kR$, with R the nuclear separation. r_{13} is the separation between electron 1 and the positron.

For overall Σ_u^+ symmetry, $c_i + d_i + s_i$ is odd and $q_i = u_i = 0$. The Hylleraas functions have $p_i = 0, t_i = 1$ and the separable and polarisation functions have $t_i = 0, w_i = 1, v_i = 2, p_i = 0$ or 1 . For the Π_u calculation $c_i + d_i + s_i$ is even. The Hylleraas functions have $p_i = q_i = 0, t_i = u_i = 1$, the separable and polarisation functions have $t_i = 0, w_i = 2, v_i = 1$. For the separable functions, three sets of values are used for p_i, q_i and u_i : $p_i = 0, q_i = 0, u_i = 1, p_i = 1, q_i = 0, u_i = 1$ and $p_i = 0, q_i = 1, u_i = 0$. The two sets of values with $q_i = 0$ are used for the polarisation functions. In both calculations the polarisation functions have either Σ_u^+ or Π_u electronic symmetry.

Discussion of Results

The Σ_u^+ wave calculation is described elsewhere¹². We find that the low-energy ($k \leq 0.1 a_0^{-1}$) behaviour is dominated by the polarisation functions: the Born approximation is approximately obeyed in this region although the phase shifts fall off slightly as k approaches $0.1 a_0^{-1}$. For higher incident energies up to $k = 1.0 a_0^{-1}$ the Hylleraas functions contribute most to the phase shifts, although the polarisation functions remain important. There is good agreement with eigenphase sums for the Σ_u^+ symmetry obtained by Danby and Tennyson¹ using the R -matrix method with a systematic treatment of intermediate and long-range polarisation using polarised pseudostates. Towards the top of the energy range the R -matrix eigenphase sums become increasingly larger than the Kohn phase shifts; this may be due to the fact that the Kohn calculation does not allow for mixing of partial waves. Both calculations predict that the contribution to the total scattering cross section from this symmetry is much too small to reduce significantly the discrepancy with experiment above 2 eV.

For the Π_u wave, the polarisation functions again dominate low energy behaviour and the Born approximation is followed for $k < 0.1 a_0^{-1}$. Above $k = 0.1 a_0^{-1}$ the polarisation functions have less influence. The phase shifts using separable and separable plus polarisation functions are slightly larger than the corresponding R -matrix eigenphase sums for the Π_u symmetry¹. As in the case of the Σ_g^+ wave², the inclusion of the Hylleraas functions substantially boosts the calculated phase shifts. The discrepancy with the experimental total cross section is significantly reduced; adding together the contributions from the Σ_g^+, Σ_u^+ and the two equivalent Π_u partial waves gives totals that are comparable with the results of Hoffman et al¹³ up to 4–5 eV.

We are currently adapting our calculations to allow for mixing of partial waves in each symmetry. This may improve results at the upper end of the energy range under consideration. The R -matrix results¹ suggest that higher symmetries give contributions to the total cross section comparable to that of the Σ_u^+ symmetry above $k = 0.4 a_0^{-1}$. We are currently adapting our work to include the Π_g symmetry.

References

1. G. Danby and J. Tennyson, *J. Phys. B* submitted (1989).
2. E. A. G. Armour and D. J. Baker, *J. Phys. B* **20**, 6105 (1987).
3. W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **46** 1426 (1967).
4. C. Schwartz, *Phys. Rev.* **124** 1468 (1961).
5. J. W. Humberston, *Adv. At. Mol. Phys.* **15** 101 (1979).
6. B. H. Bransden and C. J. Joachain, *Physics of Atoms and Molecules* (Longman, London and New York, 1983), p. 474.
7. N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, Third Edition (Oxford University Press, Oxford, 1965) p. 89.
8. E. A. G. Armour and M. Plummer, *J. Phys. B* in press (1989).
9. R. L. Armstead, *Phys. Rev.* **171** 91 (1968).
10. J. W. Humberston and R. I. Campeanu, *J. Phys. B* **13** 4907 (1980).
11. E. A. G. Armour, Low energy positron hydrogen molecule scattering. In *Positron (Electron)-Gas Scattering*, eds. W. E. Kauppila, T. S. Stein and J. M. Wadehra, (World Scientific, Singapore, 1986) p. 85.
12. E. A. G. Armour, D. J. Baker and M. Plummer, *J. Phys. B* in press (1989).
13. K. R. Hoffman, M. S. Dababneh, Y.-F. Hsieh, W. E. Kauppila, V. Pol, J. H. Smart and T. S. Stein *Phys. Rev. A* **34** 2798 (1982).

